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- (54) Tubular film for packing and casing foodstuffs, especially sausages and cheeses

(57) The invention relates to a tubular film for packing foodstuffs that in the state in which they are introduced into the tube are paste-like or fluid and that either after packing are heated to approximately 70 to 95°C or are packed in the hot, fluid state. The tubular film consists of at least one aliphatic polyamide, of which the glass transition temperature of  $\geq 321$  K in the dry state can be lowered, by moisture absorption, to 253 K, or a mixture of this polyamide with at least one ionomer resin, wherein the ionomer resin may be partly or completely replaced by a modified ethylene/vinyl acetate copolymer and/or a modified polyolefine. The tubular film according to the invention lies wrinkle-free against the contents after cooling. The tubular film is produced by shaping the plastics or plastics mixture and subjecting to biaxial stretching according to processes that are known *per se*.

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## SPECIFICATION

Tubular film for packing and casing paste-type foodstuffs, especially sausage and cheese

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The invention relates to a tubular film for packing foodstuffs that in the state in which they are introduced into the tube have a paste-type or fluid consistency and that either after packing and casing at room temperature are subject to heat treatment, such as boiling or scalding at temperatures in the range of approximately 70 to 95°C, or are packed in the hot, fluid state. The invention relates especially to a casing for boiling and scalding sausages and cheese sausages, that is to say, soft cheese packed in the shape of a sausage, which is usually introduced into the casing in the softened or fluid state.

In order to be suitable in practice, casings for foodstuffs such as boiling and scalding sausage, or cheese packed like sausage, must meet a number of requirements. The most important of these requirements are:

1) Even after the packed material (scalding sausage or soft cheese) has cooled the casing must lie wrinkle-free against this material, which has shrunk on cooling, that is to say, the casing must not be wrinkly since a wrinkled or shrivelled appearance is equated by the consumer with old food that is no longer fresh;

2) The casing must not be permanently deformed either when filled or as a result of the pressure of the contents which expand on heating, that is to say, it must retain its exact cylindrical shape and must not curve or bulge.

3) The casing must be adequately resistant to the temperatures to which it is exposed during boiling and scalding or when introducing fluid material, so that the casing does not burst or tear at these elevated temperatures. In practice the resistance to temperature must be such that the casing material still has at least 50% of its room temperature strength at temperatures up to 125°C.

4) It must be possible to gather and clip the casing without damaging it.

5) The casing should have a high degree of flexibility and a soft feel so that the operating personnel do not scrape the skin on their hands if the casing is filled manually.

6) A specific requirement of a casing for boiling and scalding sausages made by the expert is that as little as possible of the sausage jelly should be deposited between the sausage meat and the casing, since this is felt to be a serious drawback by both the meat processor and the consumer.

As yet, there are no known sausage casings made of a cheap plastics material that can be produced in a simple manner and that meet all of the above requirements.

Hitherto, collagen and paper coated with viscose have been the principal casing materials used for packing boiling and scalding sausages and cheese compositions. Although these customary commercial casings have properties ranging from good to excellent, they are very costly because they can be produced only

1) by time-consuming manufacturing steps;

2) by means of an expensive special plant;

3) with the use of strong acids and alkalis that require special handling materials.

During the manufacture of these casings, reaction products are produced that cause pollution of the environment, such as carbon disulphide in the case of viscose-coated casings. In addition, casings of this type are susceptible to decay and therefore cannot be stored indefinitely.

Also known are single-layer, unstretched plastics casings consisting of higher homopolyamides (polyamide 11 and polyamide 12) as well as plastics casings consisting of the same polyamides coextruded in two layers with polyamide 6 as outer layer.

Although these casings may be produced simply and with little pollution to the environment, they have considerable drawbacks. First, when they are filled with the sausage meat at filling pressures of 0.3 to 0.6 bar they are deformed in such a way that they are no longer exactly cylindrical, and, secondly, when boiling and scalding sausages having such a casing have cooled right through to temperatures of 3 to 5°C, as is customary in cold storage, they have a shrivelled or wrinkled appearance.

The first drawback, the deformation caused by the filling pressure, is known to the expert by the expression "mangelhafte Kalibrierung" ("lack of calibre stability") and means that goods packed in such casings cannot be used in automatic further processing or for sliced foods. The second drawback, namely the wrinkled appearance of the cooled sausage, is viewed with disfavour especially by the consumer who considers such a wrinkled product to be old and possibly contaminated. Furthermore, while the sausages are matured by hanging in the scalding chamber, an elongated "tip" forms in these casings in which the sausage jelly is deposited preferentially. This is also regarded as undesirable by the expert.

Apart from these unstretched single-layered or double-layered polyamide sausage casings, biaxially stretched sausage casings of polyethylene terephthalate (PETP), of polyvinylidene chloride copolymers (PVDC), and tubular films of higher

homopolyamides stretched monoaxially only in the longitudinal direction, belong to the State of the Art. The biaxially stretched sausage casings of PETP and PVDC do have a much improved tensile strength and calibre stability when being filled than unstretched plastics sausage casings consisting of polyamides, but result in wrinkle-free sausages only if they are subjected, after cooling, to additional heat treatment which is known to the expert as "after-shrinking".

"After-shrinking" means that the cooled sausage of a temperature of approximately 3°C is heated to above 80°C for a few seconds in a hot water bath or by hot air treatment. During this treatment, the casing shrinks and lies more closely and wrinkle-free against the sausage meat, the volume of which has been reduced by cooling. This additional after-shrinking is not, however, normally included in the known manufacturing process for boiling and scalding sausages. Consequently, this subsequent processing step, which requires additional devices and energy, is not, or not willingly, accepted by the

expert. Apart from the well-known formation, biaxially stretched sausage casing of PETP and PVDC also exhibit an unfavourable deposition phenomenon, that is to say, sausage jelly collects in considerable quantities between the sausage material and the sausage casing after maturing, which is considered a drawback by the consumer.

A further disadvantage of biaxially stretched sausage casings made of PVDC copolymers is their difficult production engineering, which is caused by the very narrow melting range of these thermoplasts necessitating the use of special machines, and by the splitting off of corrosive hydrochloric acid causing both pollution and materials handling problems.

The sausage casings made of higher homopolyamides, stretched monoaxially only in the longitudinal direction, do not have adequate transverse strength and therefore have the same drawbacks as the unstretched sausage casings as regards calibre stability and freedom from wrinkles.

The problem of the invention is therefore to provide a plastics casing for paste-type foodstuffs, especially for boiling and scalding sausages and for cheese sausage, that can be produced easily and cheaply, with little pollution, using customary plastics processing machines, and that meets the requirements described at the beginning and thus does not have the disadvantages of the known fibre-containing and non-fibre-containing plastics casings.

This problem is solved in accordance with the invention by a casing, made of a shrinkably stretched plastics material, which comprises at least one aliphatic polyamide of which the glass transition point in the dry state  $\geq 321\text{ K}$  ( $\geq 48^\circ\text{C}$ ) and can be lowered, as a function of moisture absorption, at least to  $276\text{ K}$  ( $3^\circ\text{C}$ ), preferably to  $268\text{ K}$  ( $-5^\circ\text{C}$ ) and especially to  $253\text{ K}$  ( $-20^\circ\text{C}$ ), or of a mixture of this polyamide with at least one ionomer resin and/or with a modified ethylene/vinyl acetate copolymer and/or a modified polyolefine. The glass transition point is measured according to DIN 53445 measuring the torsional module dependant on the temperature and moisture content of the sample.

Polyamides that are suitable for the purposes of the invention are all those having a glass transition point (also called glass transition temperature or glass temperature  $T_g$ , above which the plastics is soft and elastic and below which it is brittle, like glass) which is shifted by water absorption to lower temperatures of at least approximately  $0^\circ\text{C}$ .

Examples of suitable polyamides are: polyamide 6 (polycaprolactam or alternatively poly- $\epsilon$ -caproic acid amide), polyamide 7 (polyamino-oenanthic acid amide), polyamide 6,6 (polyhexamethylenedipic acid amide) and polyamide 6, 10 (polyhexamethylenesebacic acid amide).

The polyamides may be used alone or in admixture with one another; also suitable are copolymers consisting of at least two of the afore-mentioned polyamides with one another. Further suitable are copolymers and/or mixtures consisting of at least one of the afore-mentioned polyamides with polyamide 11 (polyamino-undecanoic acid amide) and/or polyamide 12 (polylaurin lactam), provided

only that the mixture and the copolymers meet the requirements of the shifting of the glass temperature.

Of the afore-mentioned polyamides, polyamide 6 is especially preferred.

For blow-extrusion purposes, polyamides having a relative viscosity in the range of approximately 2.5 to 4.5, preferably approximately 2.8 to 4.2, measured in a solution of 1 g polyamide in 100 ml 96%  $\text{H}_2\text{SO}_4$ , according to DIN 53727 are preferred.

The tubular film consisting, according to the invention, only of polyamides, polyamide mixtures or copolymers of polyamides meets all the requirements listed above and is therefore already excellently suitable for practical purposes. By adding ionomer resins and/or modified ethylene/vinyl acetate copolymers and/or modified polyolefins the properties of this tubular film may be even further improved especially as regards permeability to water vapour and gas and as regards tear propagation resistance.

Ionomer resins mean in this case direct or indirect copolymers of ethylene with an  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic acid that contain ethylene in a quantity of at least 50 mole %, and the rest up to 100% is formed by an acid derivative and/or an acid monomer of said acid, preferably in quantities of 5 to 25 mole %, calculated on the copolymer. Preferred acid derivatives are alkyl esters or acid anhydrides of said acids. Ionomer resins of this type have a melt-flow index of from approximately 0.5 to 40, preferably 0.5 to 10, and contain in uniform distribution a metal ion having an ionic valency of 1 to 3, preferably 2. Preferably at least 10% of the carboxyl groups of the acid in the copolymer are neutralised by the metal ion and are present in the ionic state.

Preferred as ionomer resins are the inorganic salts of ethylene/acrylic acid or ethylene/methacrylic acid copolymers that contain the acrylic acid or methacrylic acid, respectively, copolymerised in a quantity of approximately 2 to 25% by weight. Especially preferred inorganic salts are zinc and calcium salts. Ionomer resins of this type are marketed under the trade name Surlyn Resin No. 1650 and 1652, manufactured by Messrs. DuPont Chemical Co.

Instead of or in addition to these ionomer resins it is also possible to use special modified polyolefins. Suitable modified polyolefins are quaternary polymers that consist of approximately 71 to 90 parts by weight of ethylene, 3 to 9 parts by weight of an aliphatic ethylenically unsaturated carboxylic acid having 3 to 5 carbon atoms, approximately 1 to 20 parts by weight of an ester of an aliphatic, ethylenically unsaturated carboxylic acid having 3 to 5 carbon atoms with alcohols that contain 1 to 8 carbon atoms, and of 0.3 to 5 parts by weight, preferably 0.8 to 3 parts by weight, of isobutylene wherein the sum of the parts by weight is 100. A particularly preferred modified polyolefin of the afore-mentioned type consists of:

71 to 90 parts by weight of ethylene  
3 to 9 parts by weight of acrylic acid,  
1 to 20 parts by weight of the tert.-butyl ester of acrylic acid, and

0.8 to 3 parts by weight of isobutylene, wherein the total parts by weight is 100 and the constituents are in a polymer-bonded form.

Also suitable in addition to or instead of an ionomer resin and/or the aforesaid modified polyolefines are the plastics disclosed in DE-OS 27 21 474 and '475, the subject of which is incorporated into this application by way of reference. These plastics are known under the trade names 'Plexar' (manufacturer, Chemplex Company).

Plexars are blends of

I) graft polymers of an  $\alpha$ -olefine, preferably HDPE, which is grafted with an acyclic, isocyclic or heterocyclic acid anhydride, for example x-methylbicyclo[2,2,1]hept-5-en-2,3-dicarboxylic acid anhydride (XMNA) with either

II), EVA-copolymers, for example with vinylacetate-proportions of about 5% by weight or

II)<sub>2</sub> HDPE, LDPE or co- and terpolymers of HDPE or LDPE with propylene, butene and dienes.

The afore-mentioned graft polymer blends consist of 1 to 30, especially 3 to 12% by weight of component I, and of 99 to 70, especially 97 to 88% by weight of component II. A typical example of such a polymer blend consists of about 5% by weight of an HDPE grafted with about 1% by weight of XMNA having a melt-index of 0.8 g/10 min. as component I and 95% by weight of an EVA-copolymer having a melt-index of 1.0 g/10 min., a density of 0.929 g/ccm and a vinylacetate content of 4.7% by weight, as component II.

Another trade name of the afore-mentioned suitable types of plastics are 'Admer' (manufacturer, Mitsui Polychemicals Company, Ltd.) and 'CXA' (manufacturer, DuPont).

Details of these plastics are given in table 1.

Synthetic resin:	PLEXAR		ADMER		CXA-Resin
Manufacturer:	Chemplex-Company USA		Mitsui Polychemicals Comp. Ltd. Japan		DuPont De Nemours USA
Preferred types:	Plexar 1	Plexar 3	LF 300	LF 305	CXA 3095
Melt-flow index ASTM D 1238-57T g/10 min	1.0	3.0	1.3	1.0	1.3
density ASTM 1505-63T g/cm <sup>3</sup>	0.93	0.93	0.92	0.925	—
Vicat-softening point ASTM 1525-58T °C	90-100		92	83	90-100
chemical information	chemically modified ethylene/vinyl acetate polymers		chemically modified polyolefins		chemically modified polyolefins

In the following, the polyamides are referred to as component "A" and the ionomer resins, modified polyolefines and modified EVA-copolymers as component "B".

By admixing component B in quantities of at least 1 part by weight to a maximum of 50 parts by weight, preferably 14 to 30 parts by weight, and especially 17 to 25 parts by weight with component A, of which the quantity in the mixture is a maximum of 99 and a minimum of 50 parts by weight, preferably 86 to 70 parts by weight, especially 83 to 75 parts by weight, new properties are obtained that the individual components of the mixture do not possess on their own. It has thus surprisingly been shown that a casing produced from the mixture according to the invention is constructed from a number of layers although no coextrusion process has been used. The phenomenon of multiple layer-

ing within a monofilm can thus be observed here. A casing according to the invention that has been produced by stretching biaxially the corresponding plastics moulding composition consisting of the components A and B surprisingly has a tear propagation resistance that is ten times higher than that of the biaxially stretched component A, from which it is obvious that there is a direct connection between the observed multiple-layering in the monofilm and the increase in tear propagation resistance. This effect is most noticeable in the especially preferred range of 17 to 25 parts by weight of component B in the mixture according to the invention. Also, the plastics mixture of components A and B according to the invention is surprisingly considerably better suited to biaxial stretching than component A on its own. The improved stretching property consists, firstly, in an optically clearly determinable homogenization of

the stretching bubble, which is free from unstretched areas; secondly, a considerable reduction in the required stretching force has been observed, enabling continuous stretching over any period. The increase in the proportion of component B in the mixture according to the invention to more than 50% causes noticeable deterioration in terms of the criteria essential for its use as a casing, for example, increase in gas permeability, reduction in tensile strength and reduction in temperature resistance. Also the absolutely necessary shifting of the glass transition point from 48°C to, advantageously, -20°C is no longer possible.

The casing according to the invention furthermore has the following advantages:

1) Since it consists of a thermoplastically-processable plastics biaxially stretched in tube form that meets legal requirements regarding foodstuffs, of which the glass transition temperature may be reduced in accordance with the moisture absorption at least to 0°C, the casing lies against the contents even after complete cooling has occurred and still has an elastic tension.

2) Owing to the biaxial stretching of the casing, which is undertaken in such a way that in the stretched state the breaking stress is at least 2.5 times the breaking stress in the non-oriented, that is the unstretched, state, the stress-strain curve extending according to Hooke's elasticity law up to 10% below the breaking stress, irreversible deformation of the casing while filling and scalding the sausage, which are suspended in the boiling container, is avoided. Such a casing can withstand the customary sausage-filling pressures of 0.3 to 0.6 bar without becoming permanently deformed.

3) The casing according to the invention is also adequately resistant at high temperatures of up to approximately 125°C.

4) The casing according to the invention may be gathered and clipped without damage, since its notch impact strength retains a value of 40 to 60 Ncm/cm<sup>2</sup> to 0°C without appreciable loss.

5) The casing according to the invention has a high degree of flexibility and a soft feel.

6) The casing according to the invention meets the requirements made of it regarding permeability to water vapour and gas.

7) The casing according to the invention exhibits practically no deposit of jelly or fat between the sausage meat and the casing if the sausage meat has been produced according to a good trade process. Even with this proviso, there were always difficulties hitherto with sausage casings of thermoplastic plastics which people sought to overcome by increasing the concentration especially of protein-compatible functional groups, such as carboxyl and carbonamide groups, in the layer facing the sausage material. This increase in concentration of groups compatible with the sausage material, must be limited, however, in the known sausage casings. A concentration of more than 10% by weight of such protein-compatible functional groups weakens the strength properties in PVDC copolymers in such a manner that the filling strength and calibre stability of sausages produced in such casings can no longer

be guaranteed. The sausage casings according to the invention have from the beginning, in the most unfavourable case, a far higher concentration of carboxyl and carbonamide groups than PVDC copolymer sausage casings without the filling strength and calibre stability being adversely effected.

8) The sausage casing according to the invention has an extremely high tear propagation resistance which, depending on the proportion of the mixing component B, is up to 400 N/mm, whereas the known biaxially stretched casings of PVDC copolymers and PETP have tear propagation resistances only in the order of magnitude of 10 to 30 N/mm according to DIN 53 363.

A high tear propagation resistance is an important prerequisite especially for trouble-free vacuum packing of cut sausages. The sausage, ready for selling, is usually cut into pieces for vacuum packing purposes and these pieces are individually vacuum-packed. When a plump, wrinkle-free sausage is cut, very small tears appear in the casing at right angles to the cutting face. When a piece of sausage cut in this manner arrives at the vacuum-packing machine, the air enclosed in the porous structure of the sausage composition expands under the effect of the vacuum in such a manner that the stress on the sausage is increased considerably and if the tear propagation resistance is inadequate, this results in the tears produced by cutting tearing further. All of the hitherto known biaxially stretched plastics films, including the films of PETP and PVDC copolymers, have inadequate tear propagation resistance.

The casing according to the invention is produced by shaping the components A and B into a tubular film in a manner known *per se*, preferably in accordance with the blow film process. The polyamide, ionomer resin, modified EVA copolymer and/or modified polyolefins are mixed likewise in a manner known *per se*. Following the film manufacture, the biaxial stretching is likewise carried out according to known methods, with stretching ratios, longitudinally and transversely, in the range of approximately 1:1.5 to 1:4, the film being so stretched that in the stretched state the breaking stress is 2.5 times the breaking stress in the unstretched state and the stress-strain curve extends according to Hooke's elasticity law up to approximately 10% below the breaking stress. Preferably the so-called "Inflated bubble technique" is used for the stretching process, stretching being effected by means of a bubble filled with gas.

Following the stretching there is optionally a thermofixing treatment for the purpose of dimensional stabilisation, which is also known, and after this there may be known finishing treatments.

It is also possible, after the biaxial stretching, first of all to make the tubular film helical in shape according to a known process and then to subject it to thermofixing.

The invention is explained by the following examples:

*1 Examples without mixture component B*

*Example 1:*

Pure polycaprolactam having a relative viscosity



of 4 (measured in 1 g of granulate in 100 ml of 96% sulphuric acid at 20°C and a melting point of 220°C), is plasticised in a double screw extruder at a temperature of 260°C and extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness. After hardening the tube by cooling with precooled air, it is stretched in a stretching bubble to form a biaxially stretched tube of a wall thickness of 0.050 mm and a diameter of 60 mm, then thermofixed by blowing warm air over it and rolled up.

The surface stretching ratio is 1:9. (longitudinally: 1:2.5; transversely: 1:3.6). In the stretching process, owing to the instability of the stretching bubble, defects do occur from time to time.

The properties of this casing that are important for its use as a sausage casing, are shown in Table 2.

The flexibility (see column 12 of Table 2) of the casings according to the invention is already very good without any additional soaking, so that such a soaking process, which is considered necessary for numerous casings known in the art but which for reasons of hygiene is objected to owing to the high number of germs in the soaking bath, can be omitted. In some cases, however, the flexibility and thus the elastic property of the casing can be even further improved by soaking briefly before filling. The Table shows clearly the good properties (freedom from wrinkles, extreme flexibility, good adhesion to the sausage meat and good clipping and gathering properties), whereas the stretchability is somewhat impaired by instability of the stretching bubble.

#### Example 2:

A polyamide mixed condensation product consisting of 16 parts by weight of polycaprolactam, 55 parts by weight of polyhexamethylenedipic acid amide and 29 parts by weight of polyhexamethylenesebacic acid amide having a melting point of 160°C and a relative viscosity of 2.7 (measured in 1 g of granulate in 100 ml of 96% sulphuric acid at 20°C) is plasticised in a double screw extruder at a temperature of 210°C and is extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness.

After hardening the tube by cooling with precooled air, it is stretched by means of a stretching bubble to form a biaxially stretched tube of a wall thickness of 0.045 mm and a diameter of 66 mm, and subsequently thermofixed with hot air of approximately 120°C for 5 minutes then wound up.

The surface stretching ratio is 1:10. (longitudinally: 1:3; transversely: 1:3.3).

The properties of this casing that are important for its use as a sausage casing are shown in Table 2.

#### Example 3:

A polyamide blend (polyamide mixture) of 19 parts by weight of polycaprolactam and 81 parts by weight of polyhexamethylenedipic acid amide having a melting point of 240°C and a relative viscosity of 4.2 (measured in 1 g of granulate in 100 ml of 96% sulphuric acid at 20°C) is plasticised in a double screw extruder at 275°C and extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness.

After hardening the tube by cooling with precooled air, it is stretched by means of a stretching

bubble to form a biaxially stretched tube with a wall thickness of 0.050 mm and a diameter of 60 mm, and then thermofixed by blowing with hot air of 120°C for 3 minutes and wound up.

The surface stretching ratio is 1:9. (longitudinally: 1:3; transversely: 1:3).

The properties of this casing that are important for its use as a sausage casing are shown in Table 2.

#### Example 4, Wreath:

Customary commercial polycaprolactam with a relative viscosity of 4.0 (measured in 1 g of granulate in 96% sulphuric acid at 20°C) was plasticised in an extruder manufactured by Messrs. Leistritz, Type ESE 40, and extruded through an annular die to form a tube of 13.8 mm diameter and 360 µm wall thickness.

The resulting substantially amorphous primary tube was then biaxially stretched according to processes known *per se* and made into a wreath shape, again according to processes known *per se*.

The wreath, filled in a practical test with sausage meat, had a ring diameter of 175 mm, a skin diameter of 43 mm and a wall thickness of approximately 40 µm.

#### II Examples with mixture component B

##### Example 5:

A mixture of 75 parts by weight of customary commercial polycaprolactam granulate with a relative viscosity of 4 (measured in 1 g of granulate in 100 ml 96% sulphuric acid at 20°C) and 25 parts by weight of customary commercial ionomer resin with a melt-flow index of 5.0 as well as an ion type Zn, is mixed in a dry tumbler for 10 minutes, plasticised in a double screw extruder at 260°C and extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness. In continuous operation, this primary tube is then biaxially stretched according to processes known *per se*, thermofixed and wound up. The surface stretching ratio is 1:9.

(longitudinally: 1:3; transversely: 1:3).

A biaxially stretched tube of 0.050 mm wall thickness and 60 mm diameter is obtained.

##### Example 6

A mixture of 80 parts by weight of component A, consisting of a polyamide mixed condensation product of 50 parts by weight of polycaprolactam, 30 parts by weight of polyhexamethylenedipic acid amide, 16 parts by weight of polyhexamethylenesebacic acid amide and 4 parts by weight of polyamino-undecanoic acid amide having a relative viscosity of 2.9, and 20 parts by weight of component B of a quaternary ethylene/vinyl acetate copolymer consisting of 84.0 parts by weight of ethylene, 4.5 parts by weight of acrylic acid, 7.0 parts by weight of tertiary butyl acrylate and 1.5 parts by weight of isobutylene and having a density of 0.924 g/cm<sup>3</sup> and a melt-flow index of 0.6, is plasticised as described in Example 5 at 210°C and processed to form a biaxially stretched sausage casing with the same dimensions.

##### Example 7:

A mixture of 90 parts by weight of component A, which consists of 18 parts by weight of polycaprolactam and 82 parts by weight of polyhex-

of 4 (measured in 1 g of granulate in 100 ml of 96% sulphuric acid at 20°C and a melting point of 220°C), is plasticised in a double screw extruder at a temperature of 260°C and extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness. After hardening the tube by cooling with precooled air, it is stretched in a stretching bubble to form a biaxially stretched tube of a wall thickness of 0.050 mm and a diameter of 60 mm, then thermofixed by blowing warm air over it and rolled up. The surface stretching ratio is 1:9. (longitudinally: 1:2.5; transversely: 1:3.6). In the stretching process, owing to the instability of the stretching bubble, defects do occur from time to time.

The properties of this casing that are important for its use as a sausage casing, are shown in Table 2.

The flexibility (see column 12 of Table 2) of the casings according to the invention is already very good without any additional soaking, so that such a soaking process, which is considered necessary for numerous casings known in the art but which for reasons of hygiene is objected to owing to the high number of germs in the soaking bath, can be omitted. In some cases, however, the flexibility and thus the elastic property of the casing can be even further improved by soaking briefly before filling. The Table shows clearly the good properties (freedom from wrinkles, extreme flexibility, good adhesion to the sausage meat and good clipping and gathering properties), whereas the stretchability is somewhat impaired by instability of the stretching bubble.

#### Example 2:

A polyamide mixed condensation product consisting of 16 parts by weight of polycaprolactam, 55 parts by weight of polyhexamethylenedipic acid amide and 29 parts by weight of polyhexamethylenesebacic acid amide having a melting point of 160°C and a relative viscosity of 2.7 (measured in 1 g of granulate in 100 ml of 96% sulphuric acid at 20°C) is plasticised in a double screw extruder at a temperature of 210°C and is extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness.

After hardening the tube by cooling with precooled air, it is stretched by means of a stretching bubble to form a biaxially stretched tube of a wall thickness of 0.045 mm and a diameter of 66 mm, and subsequently thermofixed with hot air of approximately 120°C for 5 minutes then wound up.

The surface stretching ratio is 1:10. (longitudinally: 1:3; transversely: 1:3.3).

The properties of this casing that are important for its use as a sausage casing are shown in Table 2.

#### Example 3:

A polyamide blend (polyamide mixture) of 19 parts by weight of polycaprolactam and 81 parts by weight of polyhexamethylenedipic acid amide having a melting point of 240°C and a relative viscosity of 4.2 (measured in 1 g of granulate in 100 ml of 96% sulphuric acid at 20°C) is plasticised in a double screw extruder at 275°C and extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness.

After hardening the tube by cooling with precooled air, it is stretched by means of a stretching

bubble to form a biaxially stretched tube with a wall thickness of 0.050 mm and a diameter of 60 mm, and then thermofixed by blowing with hot air of 120°C for 3 minutes and wound up.

The surface stretching ratio is 1:9. (longitudinally: 1:3; transversely: 1:3).

The properties of this casing that are important for its use as a sausage casing are shown in Table 2.

#### Example 4, Wreath:

Customary commercial polycaprolactam with a relative viscosity of 4.0 (measured in 1 g of granulate in 96% sulphuric acid at 20°C) was plasticised in an extruder manufactured by Messrs. Leistritz, Type ESE 40, and extruded through an annular die to form a tube of 13.8 mm diameter and 360 µm wall thickness.

The resulting substantially amorphous primary tube was then biaxially stretched according to processes known *per se* and made into a wreath shape, again according to processes known *per se*.

The wreath, filled in a practical test with sausage meat, had a ring diameter of 175 mm, a skin diameter of 43 mm and a wall thickness of approximately 40 µm.

#### II Examples with mixture component B Example 5:

A mixture of 75 parts by weight of customary commercial polycaprolactam granulate with a relative viscosity of 4 (measured in 1 g of granulate in 100 ml 96% sulphuric acid at 20°C) and 25 parts by weight of customary commercial ionomer resin with a melt-flow index of 5.0 as well as an ion type Zn, is mixed in a dry tumbler for 10 minutes, plasticised in a double screw extruder at 260°C and extruded through an annular die to form a tube of 20 mm diameter and 0.450 mm wall thickness. In continuous operation, this primary tube is then biaxially stretched according to processes known *per se*, thermofixed and wound up. The surface stretching ratio is 1:9.

(longitudinally: 1:3; transversely: 1:3).

A biaxially stretched tube of 0.050 mm wall thickness and 60 mm diameter is obtained.

#### Example 6

A mixture of 80 parts by weight of component A, consisting of a polyamide mixed condensation product of 50 parts by weight of polycaprolactam, 30 parts by weight of polyhexamethylenedipic acid amide, 16 parts by weight of polyhexamethylenesebacic acid amide and 4 parts by weight of polyamino-undecanoic acid amide having a relative viscosity of 2.9, and 20 parts by weight of component B of a quaternary ethylene/vinyl acetate copolymer consisting of 84.0 parts by weight of ethylene, 4.5 parts by weight of acrylic acid, 7.0 parts by weight of tertiary butyl acrylate and 1.5 parts by weight of isobutylene and having a density of 0.924 g/cm<sup>3</sup> and a melt-flow index of 0.6, is plasticised as described in Example 5 at 210°C and processed to form a biaxially stretched sausage casing with the same dimensions.

#### Example 7:

A mixture of 90 parts by weight of component A, which consists of 18 parts by weight of polycaprolactam and 82 parts by weight of polyhex-

amethyleneadipic acid amid, having a relative viscosity of 4.2 and 10 parts by weight of ionomer resin with a melt-flow index of 1.4 and an ion type Zn as component B, is extruded as described in Example 5 to form a biaxially stretched, multi-layered sausage casing.

The properties of the casings according to the invention are given in Table 2 and compared with properties of sausage casings of the state of the art.

10 **Example 8, Wreath:**

A mixture consisting of

a) 83 parts by weight of customary commercial polycaprolactam with a relative viscosity of 4.0 (measured at 20°C in 1% solution in 96% sulphuric

15 acid) and

b) 17 parts by weight of customary commercial ionomer resin of the ion type Zn with a melt-flow index of 5.0

was plasticised in a double screw extruder produced by Messrs. Leistritz, Type ZSE 30/34 and extruded through an annular die to form a tube of a diameter of 13.8 mm and a wall thickness of 360  $\mu\text{m}$ .

The resulting substantially amorphous primary tube was then biaxially stretched according to processes known *per se* and shaped into a wreath, again according to processes known *per se*.

The wreath-shaped skin filled in the practical test with meat had an inner ring diameter of 175 mm, a skin diameter of 43 mm and a wall thickness of approximately 40  $\mu\text{m}$ .

The flexibility (see column 12 of Table 2) of the casings according to the invention is already very good without additional soaking, so that such a soaking in water, which is regarded as necessary for numerous casings known in the art but which for reasons of hygiene owing to the high number of germs in the soaking bath is objected to, can be omitted. In some cases, however, the flexibility and thus the elastic property of the casing can be even further improved by soaking briefly before filling.

TABLE 2  
Comparison of the technological properties of the sausage casings according to the invention  
with those of the sausage casings known in the art.

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Technological properties of sausage casing consisting of	Composition (parts by weight) A B	Breaking stress (N/mm <sup>2</sup> ) longitudinal-transverse	Tear propagation (N/mm) (DIN 5363)	Film thickness (mm)	Diameter of tubular film (mm)	Permeability to water (g/m <sup>2</sup> ·day) (DIN 53122)	Permeability to O <sub>2</sub> (cm <sup>3</sup> ·m <sup>2</sup> ·day <sup>-1</sup> ·bar)	Stretchability	Gathering property (2)	Clipping strength (3)	Flexibility assessed by feel of the casing (4)	Wrinkle formation judged optically	Adhesion to meat (mg/cm <sup>2</sup> ) (5)
PVDC Copolymer state of art	— —	47 81	35	0.050	60	2.1	7.0	—	27	21	soft	wrinkled	3
PETP-state of the art	— —	261 290	30	0.025	60	20.0	80.0	—	0	2	stiff	very wrinkled	20
Results of examples without compound B													
Example 1	100 —	150 190	20	0.050	60	50.0	10.0	limited	0	2	extremely soft	no wrinkles	125
Example 2	100 —	138 129	30	0.045	63	45.0	16.0	limited	0	2	very soft	wrinkles	103
Example 3	100 —	160 180	21	0.050	60	48.0	9.0	limited	1	2	very soft	wrinkles	118
Results of examples with compound B													
Example 5	75 25	105 120	298	0.050	60	12.0	15.0	gut	0	0	very soft	wrinkles	110
Example 6	80 20	85 100	190	0.050	60	28.0	30.0	gut	0	0	very soft	wrinkles	120
Example 7	90 10	70 90	340	0.050	60	18.0	17.0	gut	0	0	very soft	wrinkles	80

Footnote: The numbers in brackets have the following meanings:

- (1) Breaking stress measured according to DIN 53455.
- (2) On a customary gathering machine, 200 m of tubular film were gathered to form 10 tubes each of 20 m. Each tube was sealed at one end, and blown up with air at 0.3 bar to the original length. The inflated tubular film was immersed in water and the number of holes caused by the gathering were counted; this number is given in the Table.
- (3) 100 sausages were produced with the filling and clipping apparatus "FCA Super" manufactured by Messrs. Niedacker, Federal Republic of Germany. The number of points of damage to the sausage casings caused by the 200 clips put on were counted; this number is given in the Table.
- (4) Assessed after storing for 20 minutes in water at 253 K (20°C).
- (5) Measured in accordance with the method described in DT-OS 23 03 176 (pages 9 and 10).

Columns 10 and 11 — technical data concerning processing.  
Columns 12-14 — technical data concerning use.

## CLAIMS

1. Tubular film consisting of a stretchably stretched plastics material for packing and casing paste-type foodstuffs that either after packing are heated, or are packed in a hot fluid state, especially sausage casings for boiling sausages and scalding sausages and for cheese sausages, characterised in that it comprises
  - a) at least one aliphatic polyamide of which the glass transition point in the dry state  $\geq 321\text{ K}$  ( $\geq 48^\circ\text{C}$ ) and can be lowered, as a function of moisture absorption, at least to  $276\text{ K}$  ( $3^\circ\text{C}$ ), preferably  $268\text{ K}$  ( $-5^\circ\text{C}$ ) and especially  $253\text{ K}$  ( $-20^\circ\text{C}$ ) or
  - b) of a mixture of this polyamide with at least one ionomer resin and/or with a modified ethylene/vinyl acetate acid copolymer and/or a modified polyolefine.
2. Tubular film according to claim 1, characterised in that it contains as polyamide a polyamide from the group consisting of polycaprolactam, polyamino-oenanthic acid amide, polyhexamethylenedipic acid amide and polyhexamethylenesebacic acid amide or a mixture of at least two of these polyamides.
3. Tubular film according to claim 1 or 2, characterised in that it contains as polyamide a copolymer of at least two polyamides from the group consisting of polycaprolactam, polyamino-oenanthic acid amide, polyhexamethylenedipic acid amide and polyhexamethylenesebacic acid amide or a mixture of at least one of these copolymers with at least one of the these polyamides.
4. Tubular film according to one of the claims 1 to 3, characterised in that it contains as polyamide a copolymer of polyamino-undecanoic acid amide or polylaurin lactam with at least one of the polyamides from the group consisting of polycaprolactam, polyamino-oenanthic acid amide, polyhexamethylenedipic acid amide and polyhexamethylenesebacic acid amide or a mixture of at least one of these copolymers with at least one of these polyamides.
5. Tubular film according to one of claims 1 to 4, characterised in that it contains as ionomer resin a copolymer of ethylene, preferably in a quantity of at least 50 mole % calculated on the copolymer, and a  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic acid, wherein the proportion of acid monomer in the copolymers is 5 to 25 mole %, the copolymer has a melt-flow index from approximately 0.5 to approximately 40, preferably 0.5 to 10, and has uniformly distributed in it a metal ion having an ionic valency of 1 to 3, preferably 2, and wherein preferably at least 10% of the carboxyl groups of the acid are neutralised by the metal ion and are present in an ionic state.
6. Tubular film according to claim 5, characterised in that it contains as ionomer resin an ethylene/ $\alpha,\beta$ -ethylenically unsaturated mono- or dicarboxylic acid, preferably acrylic or methacrylic acid copolymer or a mixture of these copolymers, which contain said unsaturated acid in a quantity of approximately 1 to 25% by weight.
7. Tubular film according to claim 6, characterised in that in addition to the  $\alpha,\beta$ -unsaturated carboxylic acid an acid derivative, preferably an alkyl ester or an anhydride of said acid is present in the copolymer.
8. Tubular film according to one of the claims 1 to 4, characterised in that it contains as modified polyolefins quaternary polymers that consist of approximately 71 to 90 parts by weight of ethylene approximately 3 to 9 parts by weight of an aliphatic ethylenically unsaturated carboxylic acid having 3 to 5 carbon atoms approximately 1 to 20 parts by weight of  $\text{C}_1\text{-C}_6$  alkyl ester of an aliphatic, ethylenically unsaturated carboxylic acid having 3 to 5 carbon atoms and 0.3 to 5 parts by weight, preferably 0.8 to 5 parts by weight, of isobutylene, wherein the sum of the parts by weight is 100.
9. Tubular film according to claim 8, characterised in that it contains a copolymer that consists of approximately 71 to 90 parts by weight of ethylene approximately 3 to 9 parts by weight of acrylic acid approximately 1 to 20 parts by weight of the tertiary butyl ester of acrylic acid, and 0.8 to 3 parts by weight of isobutylene, wherein the sum of the parts by weight is 100.
10. Tubular film according to claims 1 to 4, characterised in that it contains in addition to or instead of an ionomer resin a polymer blend consisting of
  - I) graft polymers of an  $\alpha$ -olefine, preferably HDPE, which is grafted with an acyclic, isocyclic or heterocyclic acid anhydride, for example x-methylbicyclo[2,2,1]hept-5-en-2,3-dicarboxylic acid anhydride (XMNA) with either
  - II), EVA-copolymers, for example with vinylacetate - proportions of about 5% by weight or
  - II), HDPE, LDPE and/or co- and terpolymers of HDPE or LDPE with propylene, butene and dienes.
11. Tubular film according to claim 10, characterised in that it contains 1 to 30, preferably 3 to 12% by weight of component I and 99 to 70, preferably 97 to 88% by weight of component II.
12. Tubular film according to claims 1 to 11, characterised in that it consists of a mixture of approximately 50 to 99 parts by weight, preferably 70 to 86 parts by weight and especially 75 to 83 parts by weight of component A, and approximately 1 to 50 parts by weight, preferably 30 to 14 parts by weight and especially 25 to 17 parts by weight of component B, wherein the sum of the parts by weight is 100.
13. Tubular film according to one of the claims 1 to 12 characterised in that its breaking stress in the stretched state is at least twice its breaking stress in the unstretched state and the stress-strain curve exhibits an elastic behaviour up to approximately 10% below the breaking stress.
14. Tubular film according to one of the claims 1 to 13, characterised in that it is straight or is curved like a wreath.
15. Process for the production of a tubular film according to claims 1 to 14, characterised in that the mixture of components A and B are shaped into a tubular film and the tubular film formed is then biaxially stretched.
16. Process according to claim 15, characterised

in that the biaxial stretching is carried out using longitudinal and transverse stretching ratios that are in the range of from approximately 1:1.5 to 1:4.

17. Process according to claims 15 and 16,  
5 characterised in that, after stretching, the tubular film is subjected to a thermofixing process for the purpose of stabilising the shape.

18. Tubular film according to one of the claims 1  
to 14, characterised in that it contains as component  
10 B copolymers of ethylene with an  $\alpha,\beta$  - unsaturated carboxylic acid, especially acrylic or methacrylic acid, the amount of ethylene being at least 50% of said monomer, or terpolymers of ethylene with said  
15 unsaturated carboxylic acid and an acid derivative, preferably an alkyl ester or an acid anhydride, of said carboxylic acid, the amount of acid and acid derivative being 1 to 50% together and 1 to 25% for each acid and acid derivative.

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